Passivity Breakdown and Evolution of Localized Corrosion on Type 316L Stainless Steel

Shoufeng Yang [a], George Engelhardt [b] and Digby D. Macdonald [a]
[a] Center for Electrochemical Science and Technology
Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA
[b] OLI Systems Inc. 108 American Road, Morris Plains, NJ 07950, USA

Passivity breakdown of 316L SS in the presence of aggressive Cl^- and inhibitive NO_3^- anions has been experimentally studied and the results have been interpreted in terms of the Point Defect Model (PDM). By introducing the competitive adsorption of Cl^- and NO_3^- into surface oxygen vacancies at the passive film/solution interface, the PDM yields a critical breakdown potential (V_c) that is predicted to vary linearly with $\log[Cl^-]$, or with $\log\left(\frac{[Cl^-]}{[NO_3^-]}\right)$ [1] when nitrate ions are present, which is shown in Fig. 1. The Point Defect Model also explains the fact that the slope of V_c vs. $\log[Cl^-]$ does not change in the presence of NO_3^-, which is attributed to the quasi-equilibrium ejection of a cation from the barrier layer to form the vacancy pair $V_M V_O^{(2-\chi)\bullet}$ at the barrier layer/solution interface.

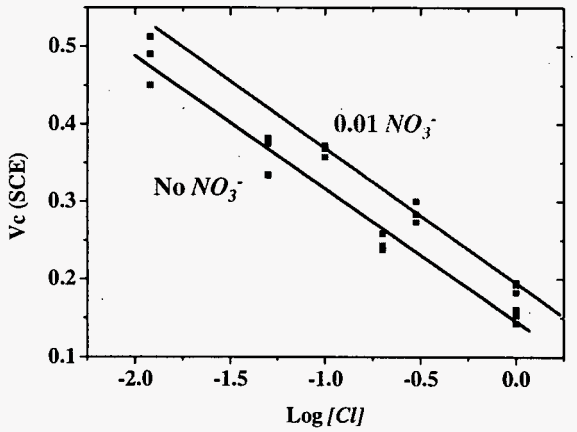

Figure 1. Critical breakdown potential vs. $Log[Cl^-]$ with or without 0.01 M $NaNO_3$

The Point Defect Model predicts that measured V_c increases linearly with the square root of voltage scan rate $\nu^{1/2}$ [1]. From this correlation, the critical, areal concentration of cation vacancies at the metal/barrier layer interface, ξ, has been estimated and found to be comparable to that calculated from the concentration of sites on the cation sublattice at the same location based on the presumed Cr_2O_3 composition of the barrier layer. The

Point Defect Model also explains the near normal distribution of V_c in terms of a normal distribution of breakdown sites on the surface with respect to the vacancy diffusivity (D) [2]. The calculated distribution agrees with the experimental results very well and this agreement is used to estimate the cation vacancy diffusivity.

Chronoamperometric studies have been performed on Type 316L SS at different voltages, $[Cl^-]$, $[NO_3^-]$ and temperatures to study the transition of metastable pits into stable pits. The survival probability for metastable pitting is determined and is used in Damage Function Analysis (DFA) to predict the accumulation of pitting damage on the surface, and is used in Deterministic Extreme Value Statistics (DEVS) to predict the distribution in the depth of the deepest pit in an ensemble of identical specimens.

References:

1. T. Haruna and D. D. Macdonald, *J. Electrochem. Soc.*, **144**, 1574 (1997).
2. D. D. Macdonald and M. Urquidi-Macdonald, *Electrochimica Acta.*, **8**, 1079 (1986).